

Electronic Supporting Information

Ionic liquid composed of purely functional sensing molecules:

Colorimetrically calcium responsive ionic liquid

Yusuke Niwa, Tatsumi Mizuta, Kenji Sueyoshi, Tatsuro Endo, Hideaki Hisamoto

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University

1-1 Gakuencho, Nakaku, Sakai, Osaka 599-8531 Japan. E-mail: hisamoto@chem.osakafu-u.ac.jp

Experimental

1. Materials

Bis(4-n-octylphenyl)phosphate calcium salt (product name: HDOPP, abbreviated here as $[\text{OP}_2\text{P}]_2\text{Ca}$) and di-n-octyl phenyl phosphonate (DOPP) were purchased from DOJINDO LABORATORIES (Tokyo, Japan). Dodecyl bromide, piperidine, lepidine, 4-methylpyridine, and 3, 5-di-*tert*-butyl-4-hydroxybenzaldehyde were purchased from Tokyo Chemical Industry (Tokyo, Japan). Dichloromethane (DCM), tetrahydrofuran (THF) and ethanol were purchased from Kanto Chemical Co. (Tokyo, Japan). Phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), calcium chloride anhydrous (CaCl_2), and disodium sulfate (Na_2SO_4) were purchased from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan).

2. Preparation of colorimetrically calcium responsive ionic liquid and membrane

2.1 Synthesis of KD-M13 and KD-M11

KD-M13 and KD-M11 were synthesized according to a previously reported method.¹

2.2 Synthesis of $[\text{KD-M13}][\text{OP}_2\text{P}]$ and $[\text{KD-M11}][\text{OP}_2\text{P}]$

KD-M13 (250 mg, 462 μmol) was dissolved to 50 mL of CH_2Cl_2 and 20 mL of 1 M H_3PO_4 was added to this solution. Then, $[\text{OP}_2\text{P}]_2\text{Ca}$ (228 mg, 231 μmol) was added to initiate the ion-exchange reaction, and the mixture was stirred overnight at room temperature. The resulting solution was washed several times with 1 M H_3PO_4 as the aqueous phase to remove residual calcium ions. After the organic phase was dried using Na_2SO_4 and evaporated, a liquid product was obtained. For $[\text{KD-M11}][\text{OP}_2\text{P}]$, exactly the same procedure to $[\text{KD-M13}][\text{OP}_2\text{P}]$ synthesis was conducted by using KD-M11 instead of KD-M13. Product was obtained as an orange solid.

2.3 Preparation of PVC membrane and a neat membrane

A mixture of PVC (4.2 mg) and [KD-M13][OP₂P] (30.6 mg; ca. 1 : 9 wt/wt) was dissolved in THF (1206 mg). The prepared THF solution was spin-coated (1600 rpm, 20 s) onto a PET film. The thickness of the PVC membrane was 240 ± 10 nm, as determined by using a laser microscope (VK-8510, KEYENCE, Osaka, Japan).

The neat membrane was prepared by a similar process but without PVC. [KD-M13][OP₂P] (36.7 mg) was dissolved in THF (1241 mg) and spin-coated in a similar manner. The thickness of the neat membrane was 170 ± 20 nm.

2.4 Synthesis of [KD-M13][N(SO₂R_{f4})₂]

Sodium bis(nonafluorobutylsulfonyl)imide (NaN(SO₂R_{f4})₂) (131 mg, 0.22 mmol) were added to the KD-M13 (114 mg, 0.22 mmol) in 50 mL of dichloromethane. To this solution, 1 M H₃PO₄ aqueous solution was added and stirred for 1 hour at room temperature. Then, the organic layer was washed several times with distilled water and dried with Na₂SO₄. After evaporation of the solvent, orange liquid was obtained.

2.5 Preparation of PVC membrane composed of [KD-M13][N(SO₂R_{f4})₂]

PVC (3.7 mg) and [KD-M13][N(SO₂R_{f4})₂] (32.1 mg) were dissolved in THF (1803.4 mg). Prepared THF cocktail was spin-coated on PET film (1600 rpm, 20 s) (Thickness of membrane : 230 ± 20 nm).

3. Preparation of conventional PVC membrane

PVC (31.4 mg), KD-M13 (2.6 mg), [OP₂P]₂Ca (2.6 mg), and DOPP(64.4 mg) were dissolved in THF (820 mg). The prepared THF solution was spin-coated (1600 rpm, 20 s) onto a PET film. The thickness of the conventional PVC membrane was 2000 ± 40 nm.

4. Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Hitachi High-Tech Science DSC7020 apparatus with liquid nitrogen cooling accessory under nitrogen gas flow. Glass transition temperatures (T_g) of [KD-M13][OP₂P] and melting points of KD-M13 and [OP₂P]₂Ca were determined by the first heating scan in the DSC measurements. The scan rate for [KD-M13][OP₂P] was 5 °C min⁻¹, and that for KD-M13 and [OP₂P]₂Ca was 10 °C min⁻¹.

Additional Supporting Data

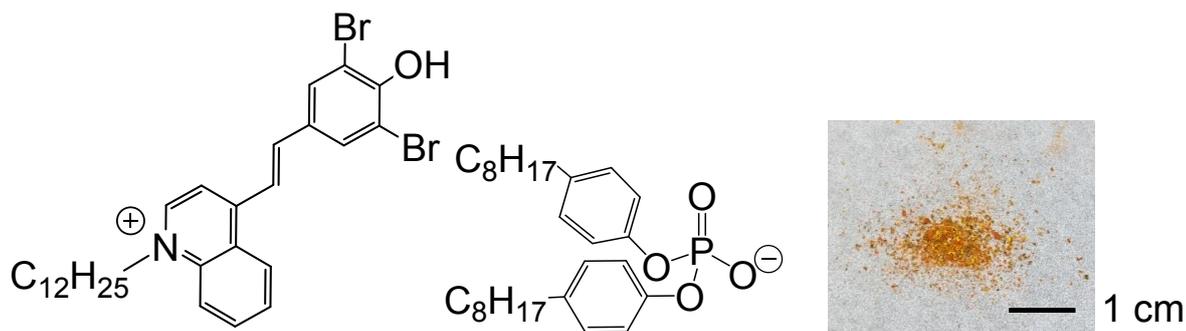
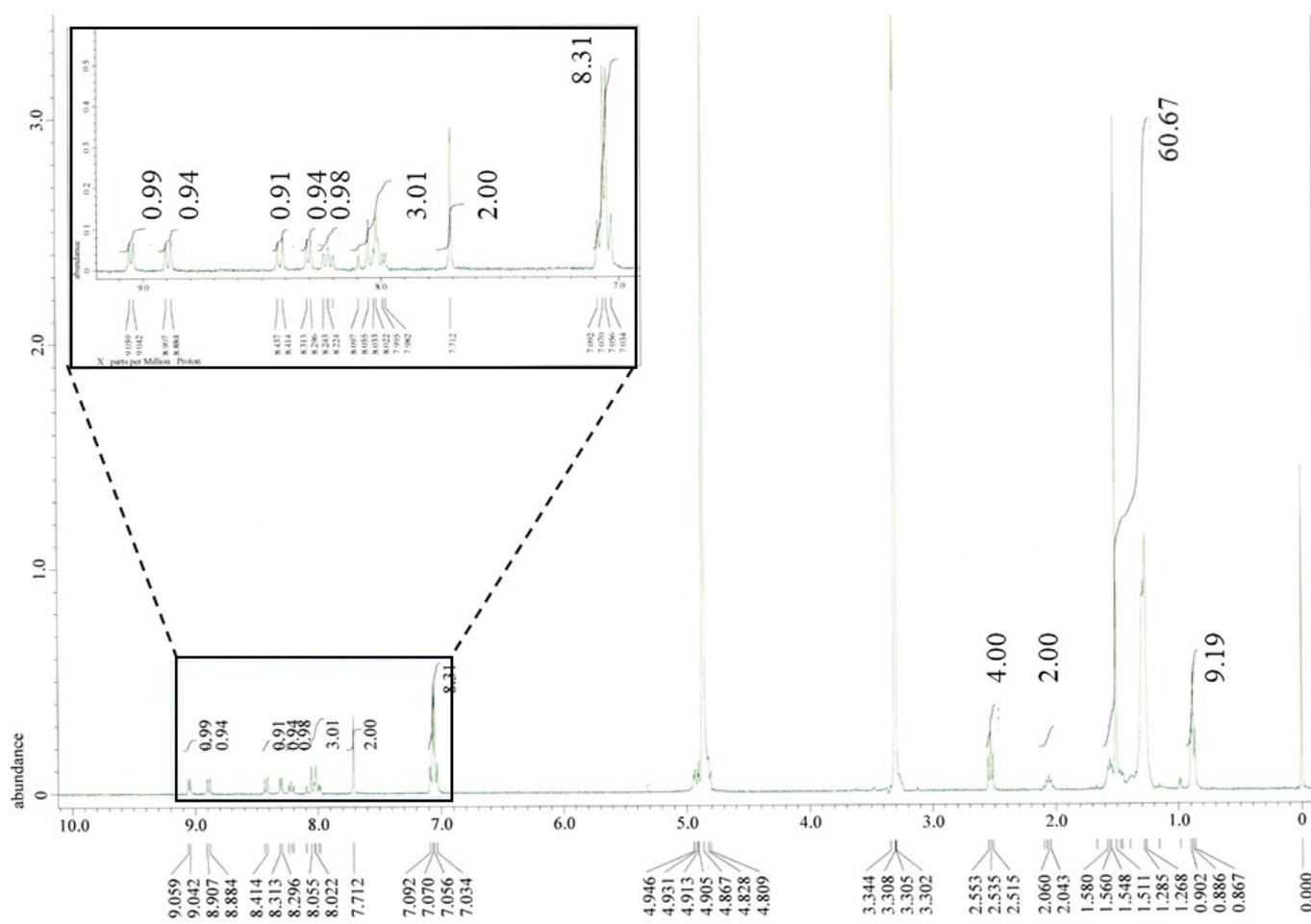


Fig. S1. Structure of [KD-M11][OP₂P], and [KD-M11][OP₂P] at 25 °C

appeared as an orange solid (scale bar represents 1 cm)



¹H NMR (400, MHz, CD₃OD) δ 0.86 (m, 9H), 1.24–1.65 (m, 60H), 2.05 (m, 2H), 2.51 (t, 4H), 7.01–7.07 (d, 8H), 7.70 (s, 2H), 7.90–8.10 (m, 3H), 8.20 (t, 1), 8.28 (d, 1H), 8.41(d, 1H), 8.89(d, 1H), 9.03(d, 1H)

Fig. S2. ¹H NMR spectrum of [KD-M13][OP₂P]

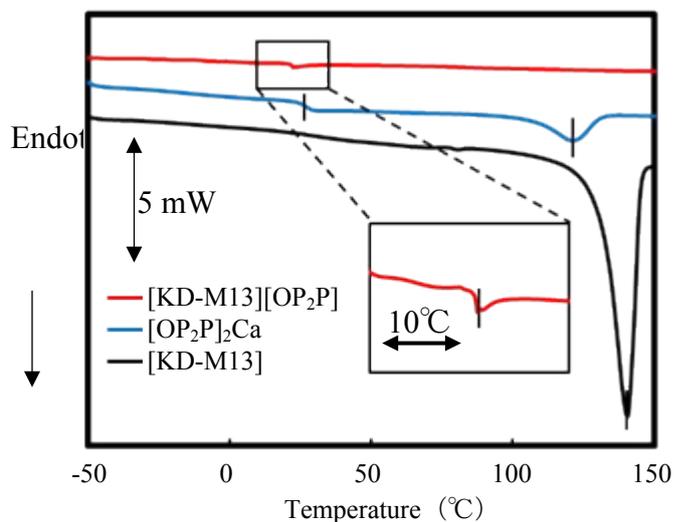


Fig. S3. Differential scanning calorimetry thermograms of [KD-M13][OP₂P] (scan rate : 5 °C/min, red), [OP₂P]Ca (scan rate : 10 °C/min, blue) and KD-M13 (scan rate : 10 °C/min, black). ([KD-M13][OP₂P] : $T_m = 22$ (°C), [OP₂P]Ca : $T_g = 27$ (°C), $T_m = 122$ (°C), KD-M13 : $T_m = 140$ (°C))

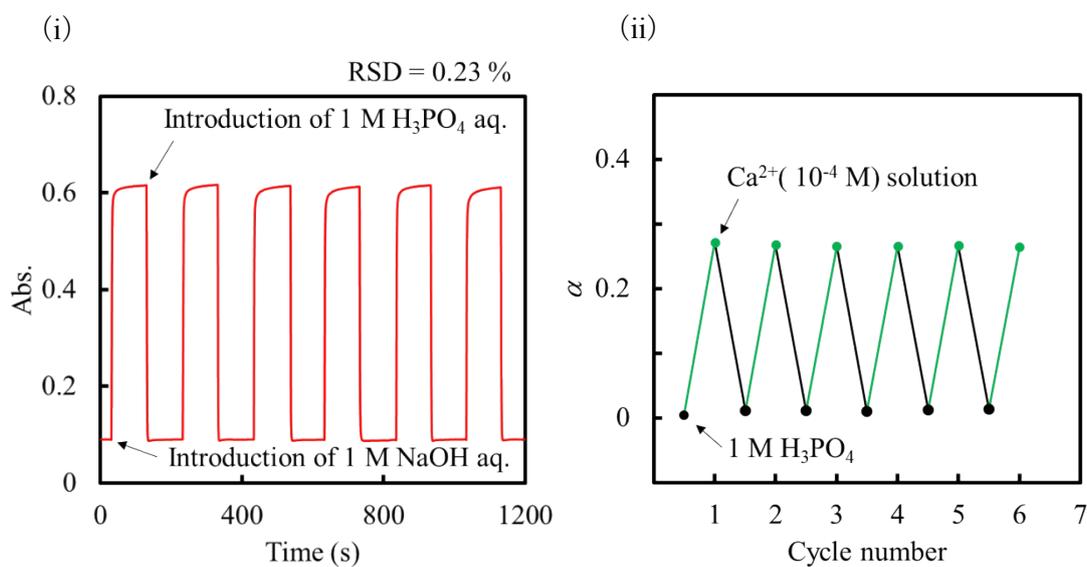


Fig. S4. Reversibility of the absorbance responses of PVC membrane at 630 nm upon introducing (i) 1 M H₃PO₄ aqueous solution and 1 M NaOH aqueous solution (ii) 1 M H₃PO₄ aqueous solution and 10⁻⁴ M calcium aqueous solution.

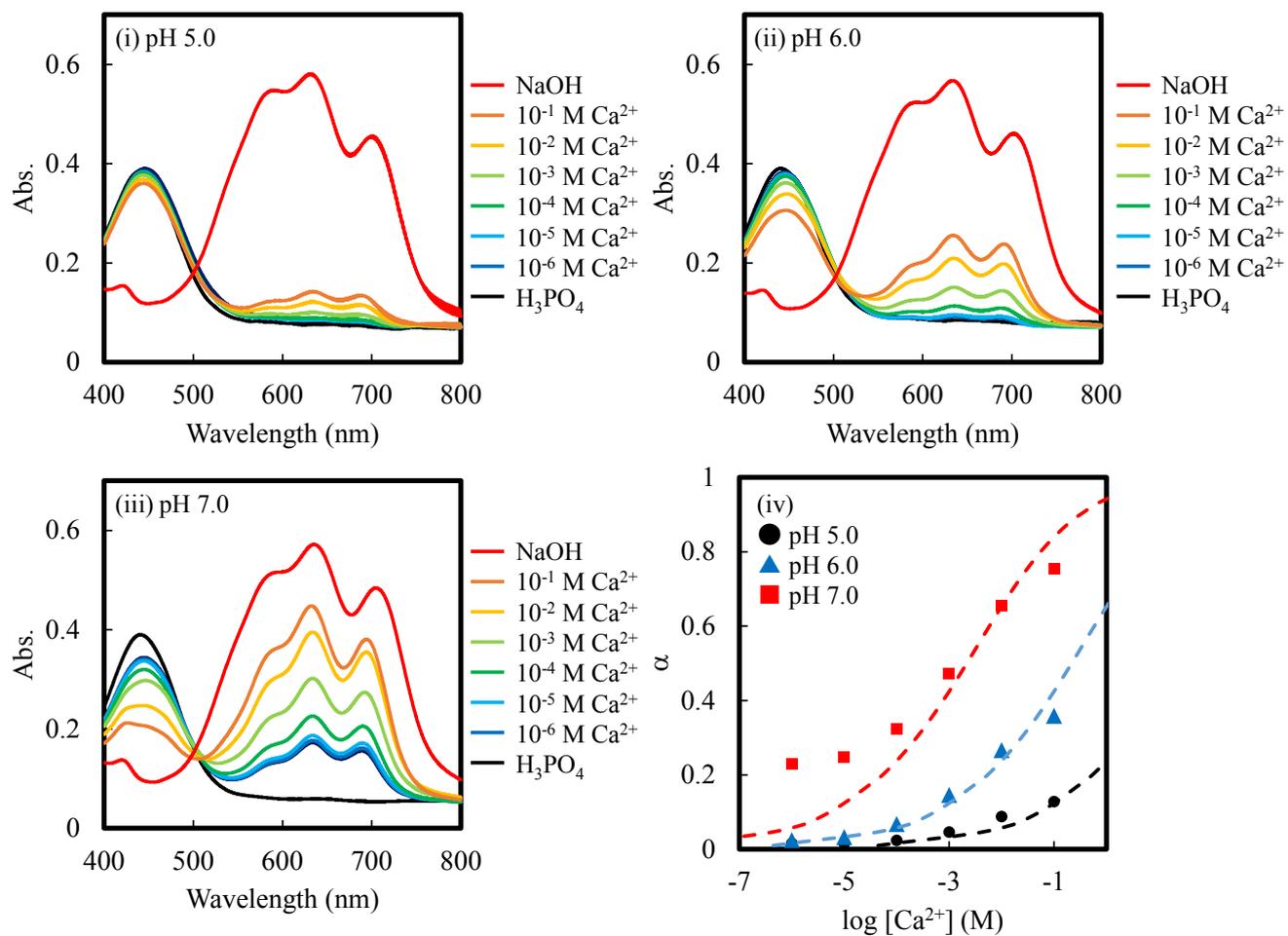
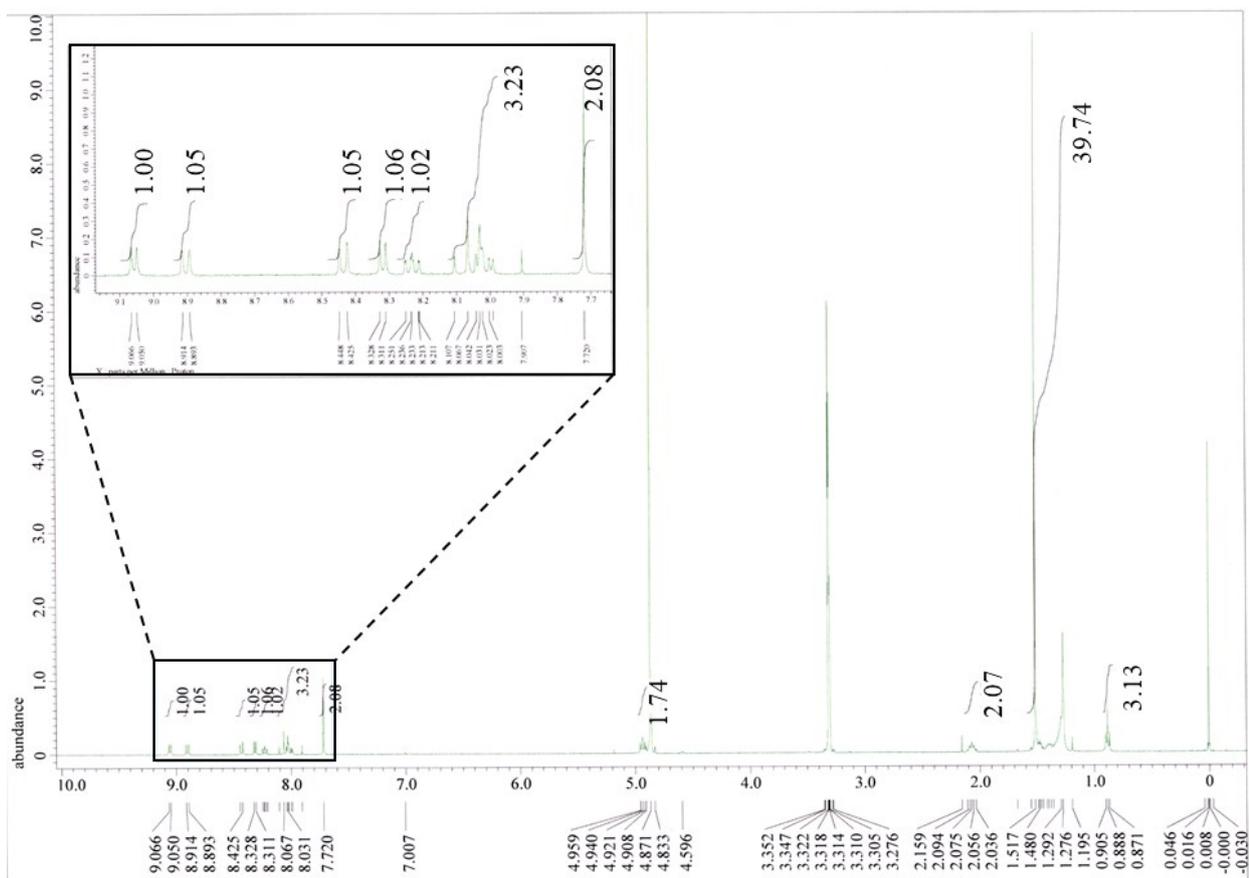


Fig. S5. Absorption spectra of [KD-M13][OP₂P]-based PVC membrane responding to several concentrations of calcium ion contained in (i) 50 mM AcOH-AcONa buffer (pH 5.0), (ii) 50 mM AcOH-AcONa buffer (pH 6.0), and (iii) 50 mM Tris-HCl buffer (pH 7.0). (iv) Response curves for each pH condition.



^1H NMR (400 MHz, CD_3OD) δ 0.88 (t, 3H), 1.24~1.65 (m, 36H), 2.08 (tt, 2H), 4.94 (t, 2H), 7.72 (s, 2H), 8.00~8.04 (m, 2H), 8.08 (d, 1H), 8.23 (td, 1H), 8.32 (d, 1H), 8.43 (d, 1H), 8.90 (d, 1H), 9.06 (d, 1H)

Fig. S6. ^1H NMR spectrum of [KD-M13] $[\text{N}(\text{SO}_2\text{Rf}_4)_2]$

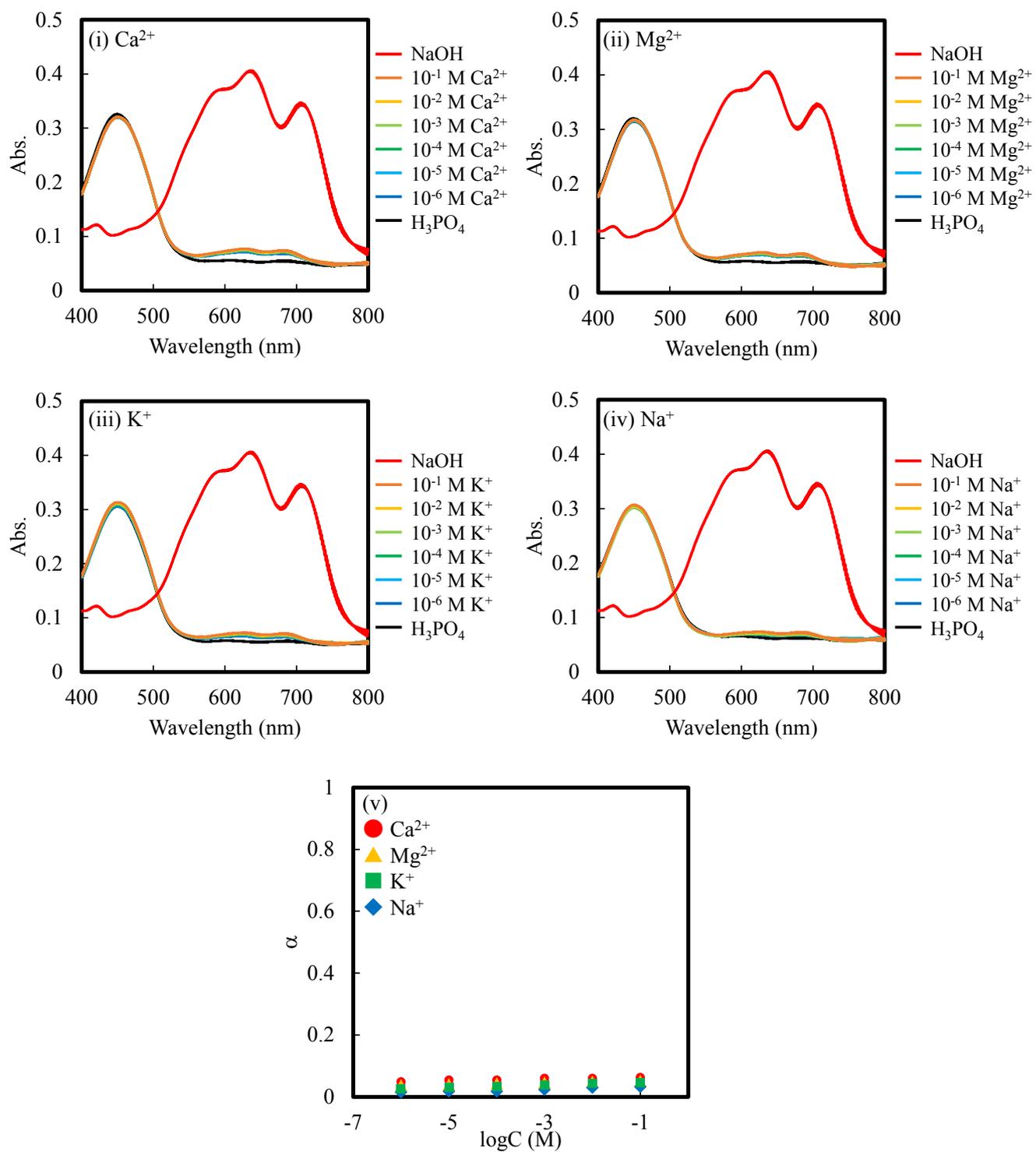


Fig. S7. Absorption spectra of [KD-M13][N(SO₂Rf₄)₂] PVC membranes for various cation solutions

((i) Ca^{2+} , (ii) Mg^{2+} , (iii) K^+ , (iv) Na^+), and response curves (v).

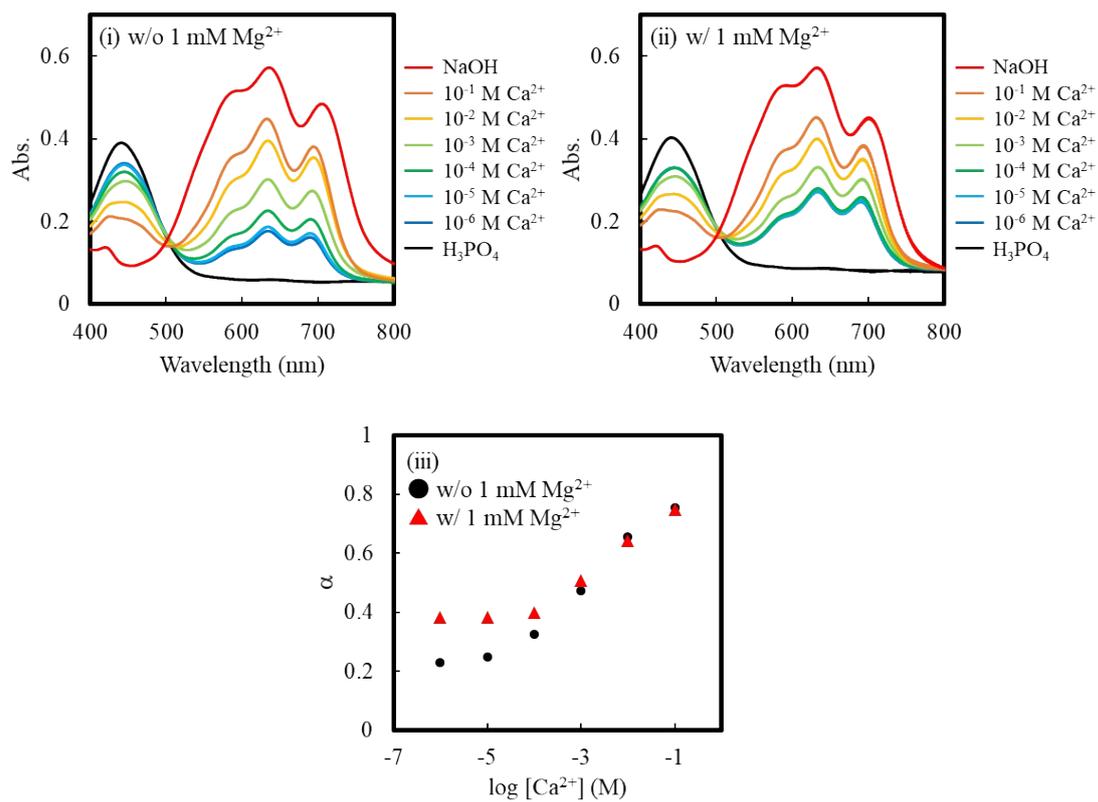


Fig. S8. Absorption spectra of [KD-M13][OP₂P]-based PVC membrane responding to several concentrations of Ca²⁺ contained in 50 mM Tris-HCl buffer (pH 7.0) (i) without 1mM Mg²⁺ and (ii) with 1 mM Mg²⁺. (iii) Response curves for each condition.

Table S1 95% Response time* of [KD-M13][OP₂P]-based PVC membrane (this work)

and conventional PVC membrane for Ca²⁺

Ca ²⁺ (M)	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴	10 ⁻³	10 ⁻²	10 ⁻¹
Conventional membrane	50 s	40 s	16 s	10 s	8.5 s	8.0 s
This work	48 s	41 s	35 s	38 s	98 s	914 s

* For the response time measurement, prepared membranes were first immersed into 1M phosphoric acid solution, followed by equilibration with buffer solution. Then, each Ca²⁺ sample solution was introduced into flow cell to obtain 95% response time.

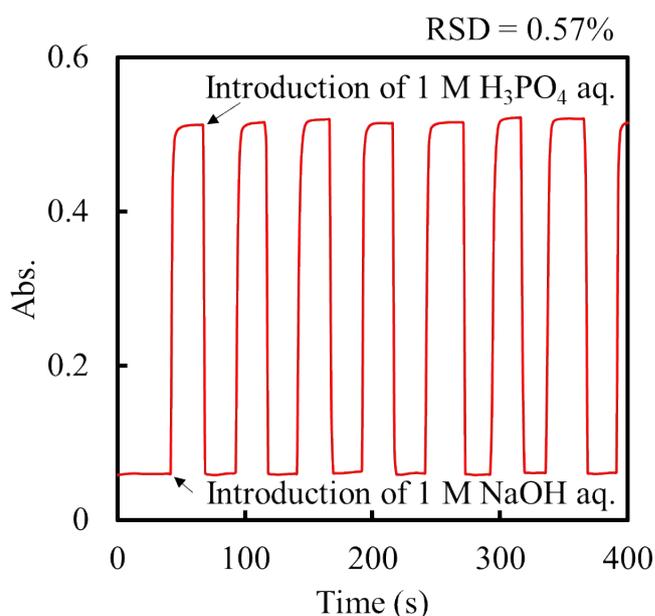


Fig. S9. Reversibility of the absorbance responses of neat membrane at 635 nm upon introducing 1 M H₃PO₄ and 1 M NaOH aqueous solution

1. H. Hisamoto, H. Tohma, T. Yamada, K. Yamauchi, D. Siswanta, N. Yoshioka and K. Suzuki, *Anal. Chim. Acta*, **1998**, 373, 271–289.